

MAGNETIC SUSCEPTIBILITY OF SOME U^{+4} COMPOUNDS AT LOW TEMPERATURES

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ABSTRACT. Magnetic susceptibility of three U^{+4} compounds have been examined over a temperature range of 400°K to 100°K. Appreciable variation of magnetic moment for U^{+4} ion from salt to salt and also with temperature has been observed for all the compounds. A theory of magnetic susceptibility based on point charge model has been worked out for U^{+4} ion in crystalline state. The calculation yields a nonmagnetic singlet as the ground state and a doublet close to it. The experimental results are satisfactorily explained.

INTRODUCTION

The magnetic properties of the actinide group of elements have received rather limited attention. In the past both the experimental and theoretical workers focussed their interest on iron and rare earth group of salts and the fine details of their magnetic properties are now well understood. In the actinides the basic confusion arose with the ground state configuration of the magnetic electrons. Dawson (1952) reviewed the magnetic susceptibility data of some of the actinide complexes and concluded that for ions with one or two electrons the $6d$ rather than $5f$ shell electrons are the important magnetic ones. His suggestion was based on the fact that many of the ions of the actinide group of compounds indicate spin only moments similar to those found in the iron group of compounds. However, Hutchison and Candela (1957) indicated that the magnetic electrons in the $5f$ shell in crystalline environment can also give rise to effective spin only value of magnetic moment. This was also confirmed from the optical absorption studies which showed similarity in the absorption spectrum with the rare earth salts in which the magnetic electrons are in the $4f$ shell. Also an analysis of U^{+4} ion spectra (Satten, *et al.* 1960) reveals that the electronic energy levels are widely separated, indicating that the crystalline stark splitting in the U^{+4} salts is large compared to the rare earth salts.

Dawson (1952), Hutchison and Candela (1957) observed a small temperature independent susceptibility for chloride complexes and a large temperature dependent susceptibility for fluoride complexes of uranium. The results were interpreted taking a six coordinated cubic field and an eight coordinated cubic field in chloride and fluoride complexes respectively. Six coordinated cubic field

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acting on U⁴⁺ ions splits the ground state $5f^2\ ^3H_4$ into four distinct levels $\Gamma_1, \Gamma_4, \Gamma_3, \Gamma_5$ (Bethe's notation, 1929) in which Γ_1 , a nonmagnetic singlet lies lowest. The next higher state Γ_4 is considerably removed from Γ_1 giving a temperature independent paramagnetic susceptibility. If the crystal field is of eight coordinated cubic symmetry then a degenerate state Γ_5 is lowest, and Γ_3, Γ_4 and Γ_1 are considerably removed from the ground level Γ_5 . The degenerate ground level contributes a temperature dependent paramagnetism and the quantitative expression is similar to a spin only value with effective spin $S' = 1$. But this simple theory does not predict a Curie-Weiss law dependence of susceptibility in UF₄ specimen observed by Leask, Osborne and Wolf (1961). Moreover, observed magnitude of the high frequency paramagnetism in UF₄ specimen has also not been confirmed by the theory. Therefore there is a discrepancy between the experimental result and the theoretical understanding of the origin of magnetism in UF₄ complexes. The present work is an extension of the earlier work of Hutchison and Candela (1957). The object has been to investigate the nature and symmetry of the crystalline field and their influence on magnetic properties of UF₄ complexes.

PREPARATION AND STRUCTURAL DATA

The complexes were prepared by photochemical reduction of uranyl ion in the presence of fluoride ion and also ammonia, hydroxylamine and hydrazine respectively, (chemicals used were of E. Merck quality). On chemical analysis they were found to possess the formula : (1) Ammonium uranium fluoride UF₄NH₄F.H₂O (2) Hydrazine uranium fluoride UF₄N₂H₄.HF(3), Hydroxylamine uranium fluoride UF₄NH₂OH.HF. They were all emerald green in colour and fine crystalline in form and insoluble in water. The coordination in the three double salts are the same as in UF₄ (Sahoo *et al.* 1961).

The x-ray crystallographic information is available for UF₄. Zachariasen (1949) has shown that the space group is C_{2h}^6 . The compound is monoclinic with 12 stoichiometric molecules per unit cell. The choice of axis corresponds to a body centered translational group. The unit cell dimensions referring to a base centered translational group and space group setting $c2/c$ are

$$a_1 = 12.79 \pm 0.06$$

$$a_2 = 10.72 \pm 0.05$$

$$a_3 = 8.39 \pm 0.05$$

and $\alpha_2 = 126^\circ 10' \pm 30'$

The positions of uranium in unit cell are $4u_1$ in $\mp(0, u, 1/4)$ with $u = 0.20$ and $8u_{II}$ in $\pm(x, y, z), (x, \bar{y}, z+1/2)$ with $x = 0.208, y = 0.437$ and $z = 0.17$. The fluorine positions are unknown.

EXPERIMENTAL METHOD

The susceptibility balance with an electronic detection system and a pair of compensating coils for balancing the magnetic force was described by Subrahmaniam (1966) in an earlier communication. The sample capsule was suspended from one arm of the magnetic balance by means of a tungsten fibre (60 S.W.G.) and its vertical position was adjusted to within ± 0.05 mm. with the aid of the electronic detection system. The sample capsule was made of Pyrex glass. The capacity of the capsule was 1/8 inch in diameter and 3/16 inch long with external dimension of 1/4 inch in diameter and 9/32 inch in length. The diamagnetic susceptibility ($\sim 10^{-7}$) of Pyrex glass capsule at room temperature showed a reduction by 10% at 80°K. The capsule was annealed at 700°K for twenty-four hours. Even then the variation was observed (3%), hence this was considered as a correction to each point in temperature variation run.

The molar susceptibility of each compound was calculated from the expression,

$$\chi_M = \chi_{M(s)} \left[\frac{M}{M_s} \cdot \frac{\Delta I}{\Delta I_s} \cdot \frac{W_s}{W} \right] \quad \dots (1)$$

and that of the U^{+4} ion in each compound by

$$\chi_M(U^{+4}) = \chi_M - \sum_i \chi_M(i)$$

where χ_M is the molar susceptibility of uranium compound and $\chi_{M(s)}$ is the molar susceptibility of the powdered $KCr(SO_4)_2 \cdot 12H_2O$ used as standard. $\sum \chi_M(i)$ is the sum of the molar diamagnetic susceptibilities of the diamagnetic constituents of the compound including diamagnetic contribution for U^{+4} (Selwood, 1956), M is the molecular weight of the uranium compound and M_s is the molecular weight of the standard $KCr(SO_4)_2 \cdot 12H_2O$, ΔI is the increment of balance compensating current for the uranium compound corrected for the capsule increment, ΔI_s is the compensating current increment for the standard sample at the standardisation temperature and at the same field, W_s is the weight of the standard sample and W is the weight of the compound. As a check of the precision of the susceptibility measurement, data on ferric alum were obtained at several temperatures down to 80°K. The deviations from Onnes and Oosterhis' values of molar susceptibility were only 0.2% at 300°K and 0.5% at 80°K.

EXPERIMENTAL RESULTS

Susceptibility measurements were made at ten different temperatures of two independent preparations of ammonium uranium fluoride, hydrazine uranium fluoride and hydroxylamine uranium fluoride. The measurement on each preparation at a given temperature represents an average of at least three determinations differing by not more than 0.1%. The data on different independent preparations have coincided too closely to be distinguished.

The results are presented in table I and the curves are drawn in Fig. 1, where the square of the effective moment

$$p_e^2 = 8.00\chi_M T. \quad \dots (2)$$

is plotted against absolute temperature T .

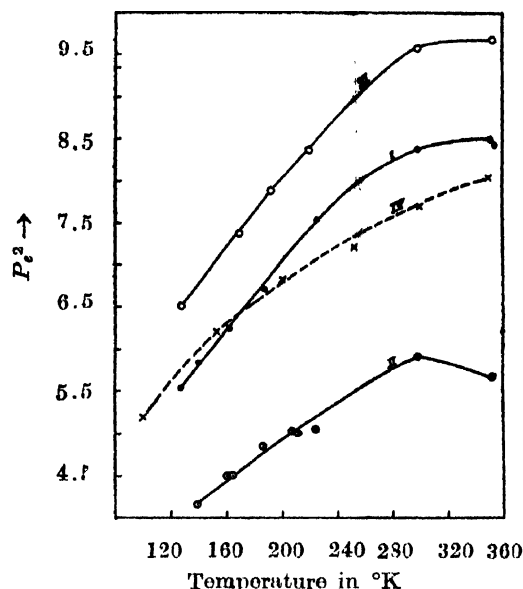


Fig. 1. Experimental curve
I. Hydrazino uranium fluoride.
II. Ammonium uranium fluoride.
III. Hydroxylamine uranium fluoride.
IV. Uf_4 data of Leask, Osborne and Wolf. (1961)

TABLE I
Temperature variation of susceptibility of U^{+4} complexes

Hydrazino uranium fluoride mass of the sample = 0.0872 gm.			Ammonium uranium fluoride mass of the sample = 0.0680 gm.			Hydroxylamine uranium fluoride mass of the sample = 0.1952 gm.		
$T^{\circ}K$	$\chi_M(U^{+4}) \times 10^6$	p_e^2	$T^{\circ}K$	$\chi(U^{+4}) \times 10^6$	p_e^2	$T^{\circ}K$	$\chi_M(U^{+4}) \times 10^6$	p_e^2
353.0	2988	8.426	353.0	2003	5.652	352.5	3438.0	9.690
351.0	3030	8.506	299.0	2488	5.947	298.0	4029.1	5.594
						220.0	4769.1	8.387
299.0	3523	8.418	224.0	2813	5.037	218.0	4809.1	8.379
227.0	4155	7.491	213.0	2899	4.938	191.0	5161.1	7.879
223.0	4203	7.539	207.0	3030	5.013	169.0	5473.1	7.394
186.0	4506	6.701	186.0	3256	4.842	127.0	6412.1	6.510
162.0	4822	6.246	165.0	3409	4.495			
139.0	5246	5.829	160.0	3526	4.509			
127.0	5459	5.543	139.0	3739	4.155			

From the Table I it is observed that for all the three salts magnetic moment corresponds to a spin only value ($p_{spin}^2 = 8.00$) at room temperature. At low temperature appreciable departure from Curie law is observed. This departure varies from salt to salt. The experimental results show temperature dependence of the type $p_s^2 = 8.00 (AT + B + C/T)$ where A , B and C are constants, representing high frequency, Curie and Weiss term respectively. Values of A , B and C giving the best fit are shown in Table II. Table II shows that there is an appreciable

TABLE II

Sample	A	B	C
U F ₄ N ₂ H ₄ HF	10.21×10^{-4}	0.8833	-40.08
U F ₄ NH ₂ OH HF	9.250×10^{-4}	1.093	-49.35
U F ₄ NH ₄ F H ₂ O	3.339×10^{-4}	0.7099	-32.42
*U F ₄	6.625×10^{-4}	0.8996	-29.985

*(Calculated from :eask,
M.J.M. Darwell, W. (1961)
(data).

high frequency contribution as well as a somewhat large Weiss term in all the salts. The high frequency contribution as well as the Weiss term varies from salt to salt. The Curie term also changes from salt to salt.

THEORY

The electronic configuration of the two odd electrons in U^{+4} ion is $5f^2$ and the Russell-Saunders coupling is large compared to crystal field effect. The spin-orbit interaction gives ground state of U^{+4} ion as $3H_4$ with an excited state $3H_5$, considerably removed from the ground state ($\sim 5000 \text{ cm}^{-1}$). The symmetry of the crystal field of U^{+4} ion is not known precisely. However, Burbank (1951) has estimated theoretically the $F-F$ and $U-F$ spacing. From the estimated structure based on chemical and packing considerations it seems reasonable that the crystal field acting on U^{+4} ion is made up of two parts :

a) a dominant part of cubic symmetry due to a regular negative charges to which fluorine atoms approximate and (b) terms of lower symmetry on account of the displacement of fluorine atoms from regular cubic position surrounding each uranium ion. The total crystal field potential acting on the central U^{+4} ion is given by,

$$V = \sum_i V(x_i, y_i, z_i) = \left(\frac{G}{20} + \frac{I_1}{4} \right) \{35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2\} + H_1 \{3J_z^2 - J(J+1)\} + \left(\frac{G}{8} - \frac{7}{8}I_1 \right) (J_+^4 + J_-^4) \dots \quad (3)$$

where the term containing G represents the part of the field with cubic symmetry and those containing H_1 and I_1 have tetragonal symmetry. Here we have neglected the sixth order cubic harmonic to simplify the calculation though this may have some contribution to the energy of the final levels. The final eigenstates and corresponding values are given by,

Wave functions	Energy
$\phi_6 = r 4\rangle + s 0\rangle + r -4\rangle$	E_6
$\phi_5 = p -1\rangle + q 3\rangle$	E_5
$\phi_5' = p 1\rangle + q -3\rangle$	
$\phi_4 = \frac{1}{\sqrt{2}} 4\rangle - \frac{1}{\sqrt{2}} -4\rangle$	E_4
$\phi_3 = r 4\rangle - s 0\rangle + r -4\rangle$	E_3
$\phi_2 = \frac{1}{\sqrt{2}} 2\rangle + \frac{1}{\sqrt{2}} -2\rangle$	E_2
$\phi_1 = p 3\rangle - q -1\rangle$	E_1
$\phi_1' = p -3\rangle - q 1\rangle$	
$\phi_0 = \frac{1}{\sqrt{2}} 2\rangle - \frac{1}{\sqrt{2}} -2\rangle$	E_0

where,

$$E_0 = -78G + 150I_1 - 8H_1$$

$$E_1 = \frac{1}{2}[(-36G - 180I_1 - 10H_1) - E_+]$$

$$E_2 = 12G - 480I_1 - 8H_1$$

$$E_3 = \frac{1}{2}[(96G + 480I_1 + 8H_1) - E_-]$$

$$E_4 = 42G + 210I_1 + 28H_1$$

$$E_5 = \frac{1}{2}[(-36G - 180I_1 - 10H_1) + E_+]$$

$$E_6 = \frac{1}{2}[(96G + 480I_1 + 8H_1) + E_-]$$

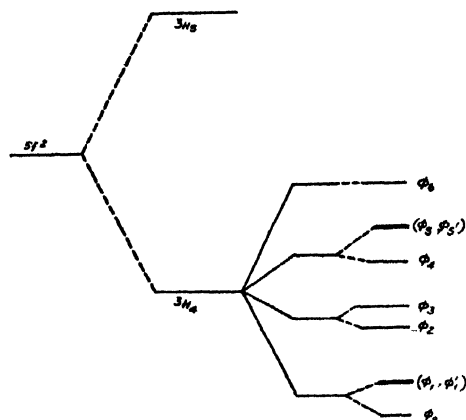
$$p = \frac{q(15\sqrt{7}G - 105\sqrt{7}I_1)}{E_1 - E_0} \quad \text{and} \quad p^2 + q^2 = 1$$

$$r = \frac{s(3\sqrt{70}G - 21\sqrt{70}I_1)}{E_3 - E_4} \quad \text{and} \quad 2r^2 + s^2 = 1$$

$$E_+ = \{(-90G - 450I_1 + 24H_1)^2 + 4(15\sqrt{7}G - 105\sqrt{7}I_1)^2\}^{\frac{1}{2}}$$

$$E_- = \{(-12G - 60I_1 + 48H_1)^2 + 8(3\sqrt{70}G - 21\sqrt{70}I_1)^2\}^{\frac{1}{2}}$$

The energy level diagram (Fig. 2) shows that the four cubic levels are split up into seven components, each triplet is breaking up into a singlet and a degenerate doublet. The cubic field leaves a degenerate triplet (ϕ_0, ϕ_1, ϕ_1') as the ground state.



Free ion + spin orbit coupling + cubic field + tetragonal field.

Fig. 2. Energy level diagram for U^{4+} ion in a tetrahedral coordination.

The tetragonal field splitting gives rise to singlet lowest (ϕ_0) and the doublet (ϕ_1, ϕ_1') is close to this ground state singlet. The other alternative of the doublet lying lowest with singlet above it is definitely ruled out because the $p_e^2 - T$ curve slopes down rapidly below room temperature (Fig. 1). p_e^2 values tend towards zero except for high frequency contribution which is an indication that ϕ_0 is lowest.

THE MAGNETIC SUSCEPTIBILITY

The first order Zeeman terms is obtained by finding

$$\langle \phi_i | H_m | \phi_j \rangle \text{ where } i, j = 0, 1, 1'$$

when $i = j$ $H_m = H_0 + \frac{4}{5} \beta H_z M_z$

and when $i \neq j$ $H_m = H_0 + \frac{4}{5} \beta H_k M_k \quad (k = x, y)$

where H_0 is the unperturbed Hamiltonian and β is the Bohr magneton. The second order Zeeman energy terms can be obtained from above by solving a secular determinant for $\phi_0, (\phi, \phi_1')$ in the usual way.

The energy in powers of the field strength H is given by

$$W_i = W_i^{(0)} + W_i^{(1)}H + W_i^{(2)}H^2 + \dots$$

where the first term is the unperturbed energy, the second and third terms are the first order and second order Zeeman energy terms respectively. Calculating the effect of the magnetic perturbation upto the second order we get the paramagnetic

gramionic susceptibility K_i ($i = \parallel$ or \perp to the tetragonal axis) using the well known formula of vanVleck.

The mean gramionic susceptibility is given by

$$\bar{K} = \frac{1}{3} (K_{\parallel} + 2K_{\perp}).$$

$$= \frac{N\beta^2 B_1}{3} \left[\frac{2A_1^2}{KT} + \frac{16D^2}{\Delta} (e^{\Delta/KT} - 1) \right] + A. \quad \dots (4)$$

where $\Delta = E_1 - E_0$ and $B_1 = \frac{1}{2 + e^{\Delta/KT}}$

and

$$A = \frac{1}{3} \frac{N\beta^2}{2 + e^{\Delta/KT}} \left[\left\{ \frac{2 \left(\frac{16}{5} pq \right)^2}{E_5 - E_1} + \frac{4 \left(\frac{2\sqrt{8}pr}{5} + \frac{2\sqrt{20}qs}{5} \right)^2}{E_3 - E_1} \right. \right. \\ \left. \left. + \frac{4 \left(\frac{2\sqrt{7}q}{5} - \frac{2\sqrt{9}p}{5} \right)^2}{E_2 - E_1} + \frac{4 \left(\frac{16}{25} p^2 \right)}{E_4 - E_1} + \frac{4 \left(\frac{4\sqrt{2}pr}{5} - \frac{4\sqrt{5}qs}{5} \right)^2}{E_6 - E_1} \right\} \right. \\ \left. + \left\{ \frac{2 \left(\frac{64}{5} \right)}{E_2 - E_0} + \frac{4 \left(\frac{2\sqrt{7}q}{5} - \frac{2\sqrt{9}p}{5} \right)^2}{E_5 - E_0} \right\} e^{\Delta/KT} \right]$$

where

$$A_1 = \left(\frac{12}{5} p^2 - \frac{4}{5} q^2 \right)$$

$$D = \left\{ \frac{1}{2} \left(\frac{2\sqrt{7}p}{5} + \frac{2\sqrt{9}q}{5} \right)^2 \right\}^{\frac{1}{2}}$$

A is the susceptibility from the high frequency contribution. The square of the effective magnetic moment can be calculated combining equation (2) and (4). The equation (4) reduces to Hutchison and Candelas' (1957) expression if the three states ϕ_0, ϕ_1, ϕ_1' are taken to be a single degenerate ground state Γ_5 . The variation of p, q with T obtained theoretically from equation (4) using the values A_1^2

$=4.00$, $D^2 = 1$ and $\Delta = 200 \text{ cm}^{-1}$ and $A = 80 \times 10^{-6}$ (p, q, r, s are taken from the cubic wave functions; in fact both A_1^2 and D^2 deviate from the above values if the magnitude of the above parameters are obtained from tetragonal wave functions) are shown in Fig. 3. The theoretical curve (Fig. 3) has been drawn with $\Delta = 200$

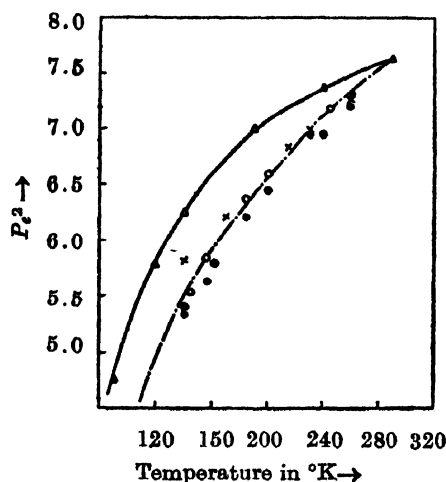


Fig. 3

————— Theoretical curve.
 - - - - - Experimental curve [room temperature value of
 all the four salts reduced to the theoretical one].

cm^{-1} as the experimental curves showed a bend near the room temperature suggesting this value of Δ . The experimental curves are redrawn in Fig. 3 reducing the room temperature values of all the three salts to the theoretical one. Points \odot , \times , \circ and \bullet given in Fig. 3 are corresponding to ammonium uranium fluoride, uranium fluoride, hydroxylamine uranium fluoride and hydrazine uranium fluoride. This procedure has been adopted because the temperature variation of p_e^2 is the same for all the three salts. The theoretical curve compares well with the temperature variation of p_e^2 for the three uranium salts (Fig. 3).

There is some divergence in the values of the Cuire constant for the three salts. It is possible that the cubic field is slightly different in them. Accurate parameter fitting can be done for the three salts; but in the absence of any magnetic anisotropy data we have not attempted such rigorous parameter fitting which in any case is not very meaningful, since the theory based on point charge model is too simple to justify a rigorous quantitative correspondence of the experimental results with the theory.

The optical absorption data of Satten, Young and Gruen (1960) refer to UCl_6 complexes which indicate that most of the excited levels lie between 5000 cm^{-1} to 29000 cm^{-1} . In all 18 pure electronic transitions are observed in the photographic region; four electronic levels are in the region 8325 cm^{-1} to 5000 cm^{-1} superimposed

with two vibronic levels. If we assign the first excited level as the most important level, the high frequency paramagnetism A is obtained to be 0.9×10^{-4} , which is one seventh of the experimentally observed value (Table II). In order to get the observed magnitude of the experimental high frequency term A at least the first excited level should be at about 1000 cm^{-1} . This difference is obviously due to the difference of coordination in chloride and fluorides as earlier indicated.

CALCULATION OF g VALUES

The values of g_{\parallel} and g_{\perp} (\parallel refers to magnetic field along Z direction which is the tetragonal axis and \perp refer to the magnetic field along the x or y direction \perp to the tetragonal axis) in terms of the admixtural coefficients are given by

$$g_{\parallel} = \frac{12}{5} p^2 - \frac{4}{5} q^2$$

$$g_{\perp} = 2 \left\{ \frac{1}{2} \left(\frac{2\sqrt{7}}{5} p + \frac{2\sqrt{9}}{5} q \right)^2 \right\}^{\frac{1}{2}}$$

The mean g value is very close to two. This compares well with resonance mean g observed at room temperature by Ghosh *et al* (1954) on powdered sample of UF_4 . g value arises from the doublet (ϕ_1, ϕ_1') states, therefore the intensity of the resonance line should drop with the lowering of temperature. Anisotropy is small and g_{\parallel} and g_{\perp} shows anisotropy if higher order admixing by the magnetic field is considered.

CONCLUSION

The most important feature of the present experimental result is that in UF_4 complexes a nonmagnetic singlet is lowest and at about 200 cm^{-1} a degenerate magnetic doublet contribute most of the susceptibility at high temperature. Such an energy spectrum evidently leads to a large temperature dependence of magnetic moment. The large high frequency paramagnetism arises from close lying levels between 1000 cm^{-1} to 5000 cm^{-1} . The g value is nearly isotropic at room temperature. The intensity of the resonance line is expected to diminish appreciably with the lowering of temperature. Up till now resonance measurements at low temperatures have not been reported.

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